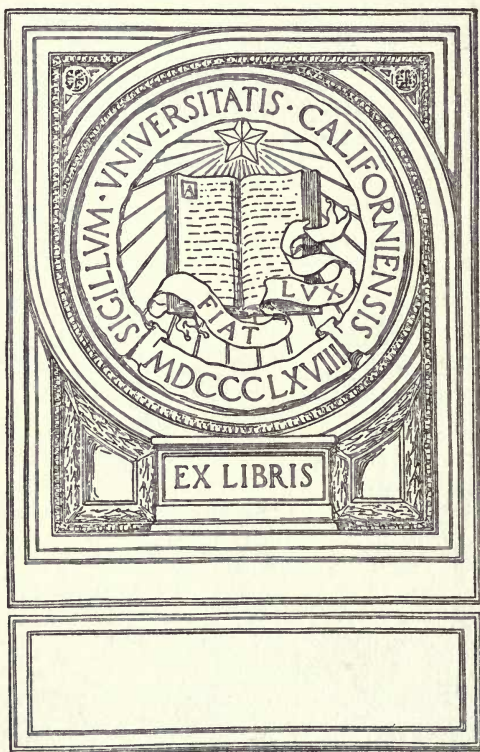


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CHEMICAL UTILIZATION OF SOUTHERN PINE WASTE

DISSERTATION

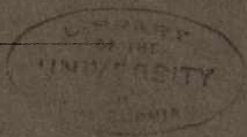
SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIRE-
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PHILOSOPHY IN THE FACULTY OF
PURE SCIENCE OF COLUMBIA
UNIVERSITY

BY

JOHN SEAMAN BATES, A.B., B.S., Chem.E.

NEW YORK CITY

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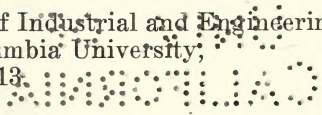
The author wishes to take this opportunity to thank those who have so kindly aided him in the carrying out of this work.

The author enjoyed the privileges of the Samuel Anthony Goldschmidt Fellowship in Chemistry for the year 1912-13, and is sincerely grateful for the aid and support thus provided.

The problem was suggested by Professor Milton C. Whitaker, and the author is deeply indebted to him for providing special apparatus and for offering valuable suggestions, criticisms and encouragement. To Dr. Otto Kress, the author is grateful for many favors. Sincere thanks are due to Mr. T. W. Pritchard, of the National Wood Products Co., Inc., Wilmington, N.C., and to Mr. J. A. Kimberly, of the Union Bag and Paper Co., Hudson Falls, N.Y., for donating the raw materials used in these investigations. Dr. L. F. Hawley, of the firm of Arthur D. Little, Inc., Boston, Mass., has lent very material aid by his critical review of the first manuscript.

J. S. B.

Laboratory of Industrial and Engineering Chemistry,
Columbia University,
June, 1913.



Chemical Utilization of Southern Pine Waste

INTRODUCTION



HERE are two phases of conservation to be considered in dealing with the forestry problem. The first involves provision for the preservation and rejuvenation of timber growth, into which enter such methods as selective cutting of trees, reforestation and prevention of forest fires. The second phase of the problem has to do with the efficient utilization of the raw materials furnished by the forest.

In the utilization of trees not fit for lumber and of the waste from forest and saw mill there is a broad field for the technical chemist. Considerable attention has been paid to these matters during the past few years and the technology of the subject is steadily advancing. The chief retarding influence is, that in spite of the enormous quantities of wood waste, the inherent value of the raw material is relatively small. The economic value of the finished products which can be manufactured from wood waste is in most cases not great and the cost of transportation and treatment of the wood is often prohibitive. The methods of utilizing wood waste differ rather widely in principle and in scope, and there are decided limitations in treating any one species of wood.

Resinous Woods

One of the most reasonable points of attack is in the direction of waste resinous woods. Several processes for the treatment of these woods are now in successful operation and others give promise of satisfactory development. The representative species are the Douglas fir, the Norway pine and the western yellow pine of the Pacific slope, and the long-leaf pine and the associated Cuban pine of the southeastern states. The species of less importance are the digger, lodgepole, sugar and pinon pines of the West, and the short-leaf and loblolly pines of the South.

The most abundant of the resinous woods and the most promising from the industrial standpoint is the long-leaf southern pine, *Pinus palustris*. As is well known, this pine is the chief wood of the southeast and holds first place among the commercial woods of the country. The utilization of the waste wood is now assuming special significance as an increasingly important factor in the naval stores industry. The virgin forests which have supplied the world with turpentine and rosin are disappearing at an alarming rate and the principles of conservation demand that the tapping and wasting of the living trees should be relieved as far as possible by the recovery of resinous products from the felled waste wood. Moreover, long continued forest operations have resulted in the accumulation of resinous waste in the forest and much of this waste has remained sound by reason of the preservative properties of the oleoresin.

The forests of long-leaf pine occupy a strip some 125 miles wide along the coast of the Atlantic and the Gulf of Mexico and constitute the main timber growth of the states from North Carolina to Texas. By reason of devastation of the forests, the turpentine centre has moved in late years from North Carolina to Florida, while the lumbering centre has advanced to Louisiana and Mississippi. It is estimated that the forest areas cover over 70 million acres and that the stand of long-leaf pine amounts to about 232 billion board feet. (U. S. Dept. Agric., Forest Service, Bull. 99, p. 8).

According to the report of the Census Bureau, the cut for the year 1910 of all eastern "yellow" pines, (of which the greater part was long-leaf pine), amounted to 14 billion board feet. This represents about two-thirds of the total cut of resinous woods throughout the entire country. The consensus of opinion seems to be that in ordinary lumber operations at least 60 per cent of the actual wood in the tree is wasted in transforming the same to sawed lumber, about 35 per cent being lost at the mills in the form of sawdust, slabs, edgings and shavings, and 25 per cent remaining in the forest in the form of tree-tops, branches, stumps, etc. (U. S. Dept. Agric., Y. B. Sep. 534, 1910, p. 257). This would signify that the waste amounted to 21 billion feet, as the census figure refers to finished lumber. Assuming 1,000 board feet to be equivalent to 1 cord, this would represent an annual production of 21 million cords of waste resinous woods in the South. The estimation by Veitch and Merrill (U. S. Dept. Agric., Bur. Chem., Bull. 159, p. 24) of 8 million cords of waste resinous woods of all kinds formed annually seems to be erroneous, as they have apparently taken the census figure as representing 100 per cent of the actual wood cut.

It is of course impossible to determine exactly the total amount of long-leaf pine waste produced each year. Furthermore, the waste varies widely in oleoresin content and a large proportion would be too lean to warrant treatment for the recovery of resinous constituents. The effective utilization of this class of wood waste by a variety of processes would surpass the present production of the country in the items of low-grade papers (other than newspaper), rosin, rosin oils, turpentine, pine oil, rosin spirits, wood tar, soft wood charcoal and ethyl alcohol.

Composition of Long-Leaf Pine

The constituents of economic value existing in long-leaf pine are the oleoresin and the wood itself. The products actually obtained from the pine depend on the methods of treatment.

The oleoresin varies widely in amount but its composition is fairly uniform, the volatile oils comprising approximately 20 per cent of the crude gum, and colophony or rosin making up the remaining 80 per cent. The volatile oils or "crude turps" yield from 60 to 80 per cent of actual turpentine and from 40 to 20 per cent of heavier oils, known collectively as "pine oil." As it exists in the wood, the turpentine consists mainly of terpenes of the formula $C_{10}H_{16}$, chiefly α -pinene with smaller amounts of β -pinene, dipentene, camphene, and traces of other oils. (U. S. Dept. Agric., Forest Service, Bull. 119, p. 7; Bur. Chem. Bull. 144, p. 21). The turpentine fraction distills between 155° and $180^{\circ}C.$, the main portion passing over close to the boiling point of pinene (155 – $156^{\circ}C.$). The pine oil consists essentially of terpineol, with small amounts of borneol, fenchyl alcohol, limonene, cineol and other terpenes and related compounds. Gum turpentine issues from the sapwood of the living tree and consists almost entirely of pinene, whereas the volatile oils of the heartwood contain appreciable amounts of dipentene and heavier oils.

The colophony or rosin consists chiefly of monobasic rosin acids. The main constituent (80–90 per cent) is believed to be abietic acid or its anhydride. Authorities differ as to the exact composition of abietic acid, some holding to the formula $C_{20}H_{30}O_2$ and others to $C_{19}H_{28}O_2$ (see Forest Service, Bull. 119, pp. 7–8 for references). There are no esters, but bodies of a lactone nature are present in small quantity as shown by the discrepancy between the saponification and acid numbers.

The true wood, (Klason, see Schwalbe, "Die Chemie der Cellulose," pp. 395 and 441; Dean and Tower, J. Am. Chem. Soc., 29, (1907), p. 1119) considered apart from oleoresin and moisture, is essentially lignocellulose, made up of 55–65 per cent of stable cellulose, $(C_6H_{10}O_5)_n$, associated in a colloidal state with about 30 per cent of lignin, a carbohydrate of uncertain composition and higher carbon content, approaching the empirical formula $C_6H_7O_3$ (Cross and Bevan

Researches on Cellulose, 3). The balance is made up of lower carbohydrates, chiefly pentosans and hexosans, and small amounts of protein and mineral ash. The moisture content of pine varies from about 5 per cent in very fat wood to 30-40 per cent or more in some classes of lean wood, average air-dry wood containing about 20 per cent of moisture. This is an important consideration in all calculations.

Classification of Wood Waste

It is well to have in mind the various classes of wood waste which are available. The mill waste, which represents about 35 per cent of the original tree, is chiefly sawdust, slabs and edgings. The sawdust is usually low in oleoresin content, because the average saw lumber is lean. Moreover, its fine state of division allows more or less volatilization of the turpentine. The slabs are available in large quantities and offer one of the most convenient forms of raw material. Their percentage of bark is of course very high and its removal is a problem to be considered. Furthermore, the slabs come from the outer sapwood of the tree, where the oleoresin content is lowest. The richest slabs are those from the "box face" of trees which have been tapped for gum spirits of turpentine. The waste remaining in the forest is abundant, but is not so accessible. Large branches, tree-tops and occasional logs left by the lumbermen afford raw material in a form compact enough for handling. Stumps usually have a high oleoresin content and offer a great bulk of solid rich wood. Their utilization is of special significance in cases where the land is being cleared for agricultural purposes. Uprooting of the stumps and perhaps freeing from dirt and roots must be taken into account. The most attractive class of forest waste is the "dead and down" material known as "light-wood." After the period of turpentine orcharding, the exhausted trees are in many cases allowed to remain until they fall. The bark and the outer sapwood decay and in five to fifteen years there is left a resinous log, which resists the natural processes of disintegration for long periods. This explains

the large supply of lightwood now available.* Lightwood is often charred by the ground fires which run through the pine forests.

Turpentine Orcharding

The oldest and most approved method of obtaining rosin and turpentine depends on making incisions in the living tree and collecting the oleoresinous exudate. This general operation is known as "orcharding." The turpentine is recovered from the crude gum by distillation and the non-volatile rosin is purified by a simple process of straining while still in a molten condition.

The "gum spirits of turpentine" so obtained are always taken as the highest standard of quality, since they are not contaminated by those decomposition products formed during certain other treatments of resinous woods. The orcharding method is simple and requires but little outlay for apparatus. The exhausted trees are available for lumber, and the choice of areas for orcharding is now usually made with this end in view. On the other hand, the yield from a single tree is small, the average being 10-12 pounds of crude gum per annum (Herty, *J. Ind. Eng. Chem.*, Jan. 1913, p. 67). This necessitates the exploitation of a very large number of trees and any but the most careful methods of orcharding result in rapid devastation of a forest.

Destructive Distillation

The aim in this process is to heat the richer grades of pine in closed retorts at progressively higher temperatures in order to first liberate the volatile oils of the wood in a comparatively unchanged condition and finally to decompose the rosin and the wood into a series of products which are for the most part volatile at high temperatures.

*A. Tschirch, in "Die Harze and die Harzbehalter," second edition, describes the increased accumulation of rosin in a wounded or dead tree as a pathological process carried on by minute organisms.

Below 200°C. the main products—moisture, turpentine and pine oil—are primary in nature. With continued increase in temperature the wood itself suffers decomposition, with formation of water and small amounts of acetic and formic acids, then light tar oils, gas and small amounts of methyl alcohol, and finally heavy tar oils; charcoal is left as a residue in the retort. At temperatures approaching 300°C. rosin begins to decompose, the successive products being water, light rosin spirits, heavier rosin oils and pitch.

The main problems in the destructive distillation process are uniform distribution of heat and accurate control of temperature. The types of retorts are numerous and differ rather widely in methods of heat application.

The fractions obtained by the destructive distillation of resinous wood are for the most part mixtures of the decomposition products of rosin and wood. Purification of the products is for this reason difficult and imperfect. The number of end products is relatively large, but many of them are of low inherent value. Destructive distillation has the advantage, however, of adapting itself to rough and even charred wood, without the necessity of finely dividing the same. Furthermore, certain valuable products, such as pine tar, tar oils and creosote, can be obtained by this process alone.

Steam Distillation

Although the boiling point range of turpentine lies above 155°C., both turpentine and pine oil are volatile with steam at temperatures above 94–96°C. The steam distillation process aims to remove the volatile oils from the wood by this simple agency. The finely divided resinous wood is subjected to the action of saturated or superheated steam in suitable retorts for several hours, until the greater portion of the crude turpentine has been carried over. The volatile oils are readily separated from the aqueous layer in the distillate and by a series of fractional distillations in a column still the end products, wood turpentine and pine oil, are isolated in a favorable state of purity.

While the principles involved in the steam distillation process are very simple, the utilization of the wood is incomplete, in that only the volatile constituents are recovered. The limitations have proved so great that nearly all the commercial plants have ceased operations within the past two or three years. It seems probable, however, that steam distillation will remain as an important step in more comprehensive treatments of resinous pine.

Extraction Processes

1. Volatile Solvents

Rosin and turpentine are soluble in a considerable number of volatile solvents, the most common of the cheaper ones being naphtha, gasolene and coke-oven benzene. The ordinary commercial solvent is a light gasolene, all fractions of which are volatile below 130–140°C. The extraction process depends on the removal of the rosin and turpentine from the finely divided wood by the agency of a solvent; the extract is subsequently distilled to recover first the solvent and finally the turpentine and pine oil, leaving the rosin as a residue.

In some cases (Walker, J. Soc. Chem. Ind., 1911, p. 394; U. S. Pat. 922,369 and Yaryan, U. S. Pats. 915,400; 964,728; 992,325), the turpentine is first removed from the shredded wood by steam distillation in order to escape the usual danger of retention of solvent by the turpentine. There is also a possibility of using the extracted wood for the production of paper pulp, although the fine state of division of the wood would detract from its value in this connection.

The main products—turpentine, pine oil and rosin—are in most respects of very favorable quality, since they are free from those decomposition products formed at higher temperatures in the other processes. The chief difficulty lies in the loss of solvent during the cycle, amounting as it does to 20–25 gallons per cord of wood extracted.

2. Alkalis

When rosin is heated with caustic soda, sodium carbonate or equivalent alkali, the rosin acids com-

bine with the alkali to form a soluble rosin soap. Turpentine and pine oil are stable in presence of dilute solutions of alkali and may be removed therefrom by distillation with steam. Wood itself is affected only in slight degree on heating with dilute alkali at low steam pressures, a small proportion of the lignin being carried into solution. These well-known facts have suggested the use of dilute alkaline solutions to effect a separation of the primary constituents of resinous wood.

A more detailed discussion of the factors entering into the extraction of resinous wood with alkalis will be found in the second part of this paper.

Bath Processes

Commercial operations on a limited scale have been carried on for some time whereby the turpentine and pine oils and incidentally part of the rosin are extracted from the wood by a hot bath of non-volatile or high boiling material. Molten rosin alone and mixtures of rosin, pitch, pine tar, pine oil, etc. have been used as baths for flooding the wood. Final injection of steam into the bath carries off the turpentine and pine oil and permits of using the bath for treating the next batch of wood. The extracted wood may be used as fuel or it may be destructively distilled.

Hydrolysis

The hydrolysis of the lignocellulose complex of wood by acids and the production of ethyl alcohol from the fermentable sugars so formed constitute a problem of ever-growing interest. Long-leaf pine has been the raw material used in a large proportion of the investigations along these lines and at least two alcohol plants in this country are now treating this wood on a large scale.

Very dilute solutions of sulphurous, sulphuric or hydrochloric acid are used as hydrolyzing agents and rather high steam pressures are necessary to effect the decomposition of the lignin and cellulose. The fermentable sugar, calculated as dextrose, amounts to 10-20 per cent of the dry weight of the wood under favorable conditions. The extract is neutralized with lime, cooled, and treated with

yeast. After fermentation is complete, the alcohol is distilled off and rectified.

The attractive feature of the process is the high yield of alcohol, a material which is becoming of more and more importance in the industries. Furthermore, it is the only process especially suited to the use of sawdust, and it does not depend for its success on the oleoresin content of the wood.

Before leaving this subject, an alternative use of the hydrolyzed wood mass should be mentioned. It has been found (Zimmerman, J. Royal Soc. Arts, 61, 1912, pp. 69-81; J. Soc. Chem. Ind. 31, p. 1197) that the sugar liquor and "pulp" formed by treating sawdust with SO_2 solution under pressure is admirably suited as a basis for a valuable cattle food.

Paper Pulp

The use of long-leaf pine for the manufacture of pulp and paper is an industrial development of recent years. Laboratory and commercial experiments on this new raw material have proved fairly successful and the indications are that a paper industry of no mean proportions will be built up in the South. Several plants are already in operation and other extensive projects are claiming the attention of pulp and paper experts.

The soda process depends on the decomposition and solution of the lignin by a caustic soda liquor at high temperature and pressure. Of perhaps more significance is the sulphate process. The presence of the sodium sulphide improves the color of the pulp and simplifies bleaching; at the same time, the fibre is smoother and firmer, and imparts better wearing qualities to the paper.

Sound, lean wood is best adapted to pulp making. In addition to the direct supply of logs, the large quantities of mill waste in the South furnish a convenient and cheap source of raw material.

To make the treatment of the more resinous classes of pine waste reasonable and profitable, attention must be given to by-products. Rosin and turpentine may be first removed by a volatile solvent (Rowley, U. S. Pat. 942,106). Several of

the methods suggested have aimed at preliminary removal of the volatile oils in a pure form by distilling at moderate pressures with steam alone (Hough, U. S. Pat. 903,859), or in presence of alkali solutions (Craighill and Kerr, U. S. Pat. 817,960). It has been claimed that part of the rosin can be melted down and tapped from the bottom of the digester (Saylor, U. S. Pat. 1,004,473; Hoskins, U. S. Pat. 770,463). The spent pulping liquors may be evaporated and destructively distilled to yield rosin spirits, pyroligneous acid, tar, etc. (U. S. Dept. Agric., Bur. Chem., Bulletin 159).

EXPERIMENTAL

Scope of Investigation

In the chemical utilization of wood waste it seems highly desirable to aim at simplicity of treatment and at the same time provide for as complete a recovery of valuable products as is economically possible. Usually one type of treatment is paramount in a plant and any complication is looked upon with disfavor. And it is quite apparent that a succession of widely varying types of treatment is not conducive to the smooth operation of a mill. A limitation of the number of end products is a decided advantage and these products should be obtained in the most direct manner and in as pure an initial form as possible.

It was with these considerations in mind that an investigation of southern pine waste was undertaken. The problem was limited to the more resinous classes of wood waste. Considering the recent demonstrations that excellent paper pulp can be obtained from long-leaf pine, it seemed advisable to employ a modified pulping treatment. This necessitated the preparation of the wood in the form of chips of the size demanded by a pulp mill. It remained to choose a method for treating the chips to separate the oleoresin from the wood itself and allow isolation of the three end products—turpentine, rosin and paper pulp.

Since rosin is readily saponified by alkalis and thereby rendered soluble in water, it was decided

to make use of this principle in extracting the rosin from the wood. A mild treatment was necessary to prevent undue attack of the actual wood by the alkali. The fact that turpentine and pine oil are volatile with steam at temperatures far below their boiling points suggested carrying out the preliminary extraction at low steam pressures, thereby allowing separation of the volatile oils. After removal of the rosin and turpentine the wood could be steamed with stronger alkali under more severe conditions, for the production of paper pulp.

In addition to the investigation of the factors affecting such a treatment of the wood, it was important to determine the quality and yields of the products and to provide for their purification.

Historical

There have been a number of suggestions for the utilization of resinous materials involving the principle of alkali extraction.

Craighill and Kerr (U. S. Patent 817,960, April 17, 1906) have patented a process by which the chipped wood is treated first with a small volume of liquor containing an amount of caustic soda "just sufficient to saponify the rosin and oils and neutralize the (volatile) acids without dissolving other extractive matters of the wood." Steam is admitted long enough to distil the terpenes; water is then added in order to submerge the chips in alkaline solution, and steaming is continued until saponification of rosin is complete. This solution is then drawn off and the chips treated with a stronger caustic solution for the production of paper pulp.

J. Aktschourin (French Patents 432,998, Aug. 5, 1911, and 433,424, Aug. 11, 1911; Ger. Pats. 248,275, July 12, 1912 and 257,015, Jan. 12, 1913) provides for the extraction of resinous material by heating with dilute alkali below 100°C. at several atmospheres pressure. The lower temperature lessens the attack of the lignin. The liquor is drawn off and cooled to precipitate a certain amount of emulsified resin and rosin soap. The filtrate

is used in digesting the fibrous material at high steam pressure for pulp.

Where turpentine is the only product desired, alkali has in some cases been added primarily to disintegrate the rosin and thereby permit a more nearly complete distillation of the volatile oils (Hough, U. S. Pat. 903,471).

Kerr (U. S. Pat. 832,863) has suggested a continuous process for the removal of turpentine and rosin from wood, the turpentine being first distilled with steam and the rosin being subsequently dissolved in alkaline liquor.

I. Preliminary Experiments

From a shipment of assorted pine waste, the "box-face slab" material was selected as being best suited to a laboratory investigation. This wood was sound and clean, and very rich and uniform in oleoresin content. When reduced to chips or shavings the wood had a strong turpentine odor and burned freely with a characteristic, smoky flame. Box-face slabs constitute a comparatively expensive and restricted source of raw material for commercial supply and the oleoresin content (30-40 per cent) is higher than that of average lightwood (15-25 per cent). This material, then, should present perhaps the severest conditions for complete extraction of rosin and turpentine, but the yields must be considered a maximum for southern pine waste.

A series of experiments was first made to determine the behaviour of the wood with alkalis under various conditions of temperature and pressure. Sample slabs were carefully cleaned by the removal of bark, rosin "scrape" and other surface material. Only the clean, inside wood was used in the investigations. Some of the wood was reduced to large chips—about 1 in. x $\frac{3}{4}$ in. x $\frac{1}{8}$ in., some to small chips—about $\frac{1}{2}$ in. x $\frac{1}{4}$ in. x $\frac{1}{32}$ in.—and another portion to thin shavings.

The action of volatile solvents was of course rapid and simple. Shavings and small chips were readily freed from rosin and turpentine by extraction in a Soxhlet, leaving the wood clean and de-

cidedly whiter in color. The slow penetration in the case of the larger chips pointed to the difficulties which would be encountered in using this type of treatment on chips of the normal pulping size. Ether, gasoline, ligroin and petroleum ether all yielded clear, bright yellow rosin, showing the excellent quality of the rosin as it existed in the wood. Ethyl alcohol, methyl alcohol, and acetone showed slightly greater extractive powers, the rosin, however, being deeper in color and somewhat cloudy. Ether is the most satisfactory solvent for rosin, the solubility being 38–39 per cent at 23°C. (H. A. Loos, "A Study on Colophony Rosin," Columbia University, 1900), and was used in subsequent quantitative determinations.

Extraction with alkalis is different in principle. The rosin is saponified and dissolved as a soap, while the turpentine is liberated from the rosin without itself dissolving in the alkaline solution. An important consideration is that the alkali causes partial decomposition of the wood itself. The lignone group of the wood is converted by alkaline solutions at elevated temperatures into soluble derivatives, which are acid in nature but of somewhat uncertain composition (Cross and Bevan, "Wood Pulp and its Uses," p. 62). This principle is carried to the limit in ordinary pulping operations, where the final pulp consists of cellulose practically free from lignin. Heating the wood in dilute caustic solutions at the moderate temperatures necessary for rosin extraction represents the initial stage of lignin decomposition. The dissolved bodies from this source consist mainly of organic acids of the type of saccharinic and isosaccharinic acids, as well as those of a lower order, such as formic and acetic acids. In addition, there are dissolved those water-soluble bodies and lower carbohydrates, which exist in the wood to the extent of 5–10 per cent—chiefly pentosans and hexosans, such as the glucosides of xylose, mannose, etc. (see Klason and Segerfelt, *Papierfabrikant*, 9, 1911, pp. 1093–9). For convenience, the decomposition products of the lignin of the wood will be designated as "humus" throughout the discussion.

Extraction of Rosin-free Wood with Alkali

To study the behaviour of the humus, pine shavings were first extracted with ether and then heated with dilute solutions of caustic soda. The alkali extracts were clear, and brown or cherry red in color.

Addition of excess caustic soda caused no precipitation of the organic bodies. The same was true of treatment with sodium chloride. Barium chloride gave a fine, brown precipitate of the barium salts of the humic acids, leaving a pale orange-colored supernatant liquor. Titration with mineral acids gave no precipitate up to the sodium bicarbonate stage (phenolphthalein end-point). On fully acidifying, there resulted almost complete precipitation of the humus, due to the breaking up of the sodium salts. The humus was brown, granular and easily washed by water. Only a trace proved soluble in ether, but the mass became somewhat gelatinous. After acidifying a portion of the alkali extract to the sodium bicarbonate stage, CO_2 was passed through the solution. A large proportion of the humus was precipitated. (see Rinman, U. S. Patents 1,005,882, 1,017,320 and 1,045,889, and J. Soc. Chem. Ind., 31, p. 183).

Extraction of Resinous Wood with Alkali

The behaviour of the resinous wood with alkalis is modified by the presence of rosin and turpentine. Dilute caustic soda and sodium carbonate showed little action on resinous shavings or chips in the cold. Shavings were readily extracted, however, by heating at 70–100°C. Chips were much more resistant, although the small chips were thoroughly extracted on boiling with dilute caustic soda for $1\frac{1}{2}$ –2 hours, accompanied by evolution of turpentine.

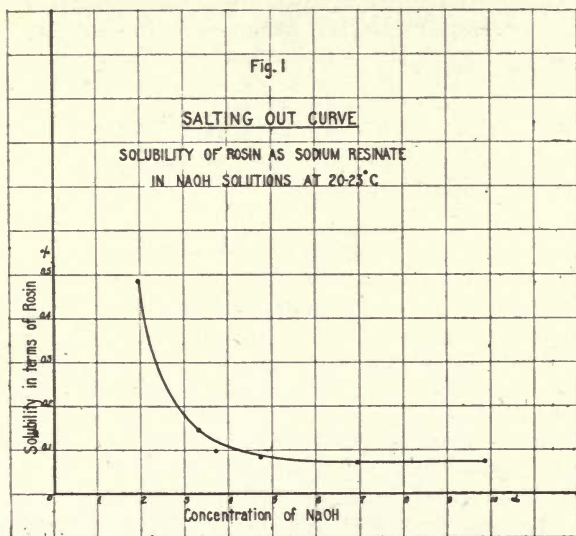
The brown extracts consisted mainly of sodium resinate and the sodium salts of humic acids. Addition of excess caustic soda in the cold caused precipitation of most of the rosin soap, which carried down some of the humus mechanically. Sodium chloride gave the same general action. Barium chloride gave a precipitate of the barium salts of both the rosin and humic acids. As in the case

of the pure wood extract, mineral acids gave no precipitate on titrating to the phenolphthalein end-point. Further additions precipitated rosin and humus together, the small quantity of humus being entrapped by the gummy rosin. Direct melting of the precipitate gave bright rosin, with humus particles disseminated throughout. Extraction with ether involved some difficulty in separating the ether layer from the gelatinous humus, but yielded a clean rosin of pale brown color. On saturating the alkali extract with CO_2 , partial precipitation of both rosin and humus took place.

The "Salting-Out" Method for Isolation of Rosin

Isolation of the rosin content of the alkali extract was most conveniently accomplished by salting out the rosin soap with caustic soda. Sodium chloride was apparently just as effective, but rather complicated the process by the introduction of another reagent. The caustic soda method was chosen because direct and simple. Humus itself is soluble in alkaline solution, but a small part is carried down by the colloidal soap. Sodium resinate is quite soluble in hot alkaline solutions, as well as in neutral or faintly alkaline solutions in the cold, but is only slightly soluble in cold alkaline solutions when the concentration of free caustic soda exceeds about 4 per cent. This solubility determines the loss in recovery of the soap. The method has the advantage of utilizing the same reagent as is employed for extracting the wood and cooking for pulp. No acid is necessary for precipitating the free rosin, if the soap is to be used as such, and no acid-resisting apparatus need be provided. The alkali used in extracting the wood and precipitating the soap can be saved partly in the form of sodium resinate (thereby enhancing the value of the rosin fraction), and partly in the form of brown, supernatant liquor to be used as a source of alkali for the soda cook of the extracted chips. After the pulping operation, the alkali can be recovered in the usual way by evaporating, incinerating and causticizing the waste soda liquor.

As regards actual manipulation, it was found best to add the excess of caustic soda to the hot extract, so that precipitation of the soap took place rather slowly as the solution cooled down. Very strong alkali—above 10 per cent NaOH—gave somewhat syrupy solutions, with increased contamination of the soap by humus and without appreciable gain in the quantity of soap precipitated. The soap precipitate proved difficult to filter. The liquor was separated by draining or syphoning. With this procedure the soft precipitate retained an appreciable quantity of liquor. The bulk of the humus was removed from the soap by dissolving the same in the minimum amount of hot water and salting out again with caustic soda.



To determine the power of caustic soda in salting out rosin soap, a series of experiments were carried on with pure rosin on a quantitative scale. The results are summarized in Figure 1.

Clear, bright rosin, prepared by extracting a good grade of paper-maker's rosin with ether, was powdered and dissolved in a slight excess of warm, dilute caustic soda solution. Separate portions of

this strong rosin soap solution were diluted with water and treated while warm with varying quantities of strong NaOH solution, so that part of the sodium resinate was in each case salted out. The solutions were placed in stoppered bottles and allowed to stand overnight to come to room temperature (20–23°C.) and to assume a state of saturation at that temperature. The solutions were then filtered, giving clear, pale-yellow filtrates. 400 cc. portions were acidified and shaken with ether to determine the rosin content. The results have been expressed in percentage strength of the solutions in terms of rosin (present as soluble rosin soap). The figures also represent solubility of rosin in grams per 100 cc. The balance of the solution was in each case titrated with standard H_2SO_4 , using methyl orange as indicator. The results represent the total alkali expressed in terms of NaOH. The error due to the precipitation of free rosin by the acid is practically negligible. The actual causticity of the alkali varied from 95 to 97 per cent, small quantities of sodium carbonate being unavoidably present.

The results are not strictly accurate or comparable with one another. This is apparent, because of the presence of sodium carbonate in the caustic solutions and because of the slight differences in temperature. Furthermore, the quantity of soap precipitated out may have had some influence on the solution itself, by reason of the colloidal tendency of sodium resinate. However, the general effect of increasing the strength of the caustic soda is quite apparent. The solubility of rosin soap in 1 per cent NaOH amounted to several grams per 100 cc., and for this reason was not determined. In 1.98 per cent NaOH the solubility was 0.4817 grams per 100 cc., while in 3.33 per cent caustic it dropped to 0.1445 grams. After a concentration of about 4 per cent NaOH was reached there was no pronounced decrease in solubility of the rosin soap; 10 per cent NaOH gave no more complete precipitation than 7 per cent caustic. This shows that rosin soap can be effectively salted out by strengthening the solution to 4 per cent NaOH

or more, thereby leaving a supernatant liquor which would be of a convenient concentration for cooking the extracted chips for pulp.

A few quantitative determinations with sodium carbonate and sodium chloride showed that these reagents had practically the same salting out power as caustic soda when compared on an equivalent weight basis.

In applying the salting out method to the alkali extracts from resinous wood, it was found that the presence of dissolved humus, etc., increased to a slight degree the solubility of the rosin soap in the strong alkali.

Extraction of Resinous Pine with Alkalis

Temperature, pressure and nature of alkali proved to be important factors in the extraction of rosin and turpentine from the wood.

EXPERIMENTS WITH CAUSTIC SODA

1. Atmospheric Pressure

Taking into consideration the necessity for steam distillation of the crude turpentine, little attention was given to extraction at temperatures much below 100°C.

Shavings heated at 100°C. in a dilute solution of NaOH, containing 1.5 times the amount of caustic theoretically necessary for saponification of the rosin in the weight of wood used, were completely extracted within 1 hour. This was determined by thoroughly washing the shavings with hot water, drying and extracting with ether. On the other hand, the largest chips (1 in. x $\frac{3}{4}$ in. x $\frac{1}{8}$ in.) were imperfectly extracted by treating at the boiling temperature with twice the theoretical amount of NaOH for a much longer period. The small chips were thoroughly extracted when 3 times the calculated amount of NaOH was used. The larger chips not only retarded the penetration of the alkali, but occasioned greater neutralization of the caustic before penetration was complete, by reason of the longer time of contact with the alkali and

more extended decomposition of lignocellulose. The extracts were much darker on this account.

2. Heating Under Pressure.

For the preliminary experiments at elevated temperatures a small autoclave of about 1500 cc. capacity was used. The autoclave was fitted with a pressure gage, thermometer pocket and relief line leading to a condenser.

With shavings the evolution of turpentine commenced as soon as pressure was evidenced and the main bulk of the volatile oils distilled over with a low ratio of water vapor in a very few minutes. In about half an hour the yield of turpentine amounted to approximately 35 gallons per cord. Later experiments showed that the true turpentine content of the wood was about 45 gallons per cord. Frothing was excessive, especially during rapid evolution of the turpentine and care was necessary in controlling the relief line. Extraction of rosin was rapid and the extracts were noticeably darker than those obtained below 100°. The caramel odor detected in all the alkaline extracts was more pronounced in this case.

3. Vacuum Treatment

The apparatus used consisted of a hemispherical porcelain bowl of about 4 liters capacity, set in a water bath and surmounted by a convex glass cover resting on a rubber gasket. A thermometer was inserted in the top and the delivery tube was connected to a condenser and receiving flask, the side tube of the latter being attached to a manometer and suction pump.

500 grams of thin chips were treated with 2500 cc. of 2.4 per cent NaOH solution, calculated to supply 3 times the amount of alkali necessary for saponification. The water bath and suction pump were first adjusted to carry on distillation at a high vacuum—20-25 inches—so that the temperature could be held below 70°C. The action of the caustic was not very rapid.

Frothing was excessive while turpentine was being evolved and constant attention was necessary

to prevent surging over of the liquor. After four hours heating the distillate measured 165 cc., containing 28 cc. of water white, sweet-smelling turpentine, which represented a yield of 27 gallons per cord. The recovery of volatile oils was incomplete and undoubtedly the distillate contained only the lighter fractions. At this stage the chips seemed pretty well extracted. A sample of the alkali extract gave a very clean, white precipitate of rosin soap on cooling, and the supernatant liquor was transparent and light cherry red in color.

The main portion was heated for some time longer under about 8in. vacuum, and distillation proceeded much more rapidly at 85—90°. A small additional amount of turpentine was obtained bringing the yield up to 30 gallons per cord. The liquor assumed a decidedly darker color, but the rosin soap precipitate was much cleaner than in the previous experiments.

EXPERIMENTS WITH SODIUM CARBONATE

Sodium carbonate was tried as an extracting agent in the hope that the attack of the lignocellulose would be minimized and solution of the rosin accomplished satisfactorily.

1. Atmospheric Pressure

Shavings were readily extracted by dilute solutions of sodium carbonate at temperatures approaching the boiling point. The action was slow at lower temperatures, but when shavings were added to a boiling solution of carbonate there was instantaneous action, evidenced by vigorous frothing due to evolution of CO_2 and turpentine. After boiling for three hours the solution was cooled, giving a clean-looking rosin soap precipitate and a transparent reddish liquor. It was found that the extracts were decidedly freer from humus than in the case of NaOH , but all the solutions were brown and the problem of humus contamination was only one of degree.

2. Heating Under Pressure

To determine the effect of pressure, 3000 grams of

thin chips were heated in the auto-clave with 1100 cc. of 4.5 per cent Na_2CO_3 solution, containing 3 times the amount of Na_2O theoretically necessary for saponification. In $\frac{1}{2}$ hour the temperature reached 100°C . and in the next 15 minutes, while the pressure rose to 30 pounds, 16 cc. of turpentine distilled over, equivalent to 26 gallons per cord. The heating was continued for a total of $2\frac{1}{2}$ hours up to 45 pounds pressure. The combined "turps" represented a yield of 33 gallons per cord. The final extract was dark brown, showing that carbonate even at low pressures has a decided action on the lignin. On cooling, the soap precipitate was whiter than in the case of NaOH .

3. Vacuum Treatment

250 grams of thin chips were heated in the vacuum apparatus with 1500 cc. of 2.7 per cent carbonate solution (3 times theory). As low temperatures were ineffective, the water bath was kept boiling. After an hour or more at atmospheric pressure the solution was yellowish and considerable rosin was dissolved. Distillation was then carried on under a vacuum of 12–15 inches and water vapor and volatile oils came over at 78 – 82°C . Even after 4 hours the yield of turps only represented 15 gallons per cord. The liquor gave a very white precipitate of soap on cooling and the solution was perfectly transparent. However, removal of the turpentine was far from being complete.

In general, then, caustic soda seemed to be the more effective agent for extraction. Sodium Carbonate gave lighter extracts and somewhat cleaner soap precipitates, but penetration of the wood was incomplete and frothing rather more pronounced. Elevated temperatures and pressures facilitated the removal of rosin and turpentine, but occasioned greater attack of the wood itself. The size of the wood units proved to be a highly important factor in extraction of the oleoresin. A fine state of division—represented by the shavings—greatly simplified the problem of extraction. On the other hand, the production of good paper pulp necessitates the preparation of the wood in chip form.

Production of Pulp

Preliminary experiments were made to determine the nature of the pulp obtainable from the box-face slab material. The cooking was done in the autoclave described above, the apparatus being standardized by the use of commercial spruce chips. Caustic soda was employed as cooking agent. The washed pulp was disintegrated in a small experimental beater and sample sheets were made up on a hand frame and in a wire stamp. The sheets were dried on a steam-heated dryer-roll designed for the purpose and in some cases finished on a gas-heated calender roll. In this way a rough idea could be obtained of the relative merits of the different pulps for the production of paper.

Without going into detail, it was found that fibre of good quality was obtainable from the resinous long-leaf pine. Shavings gave low yields of rather short and non-uniform fibre, showing the necessity of preparing the wood in chip form. The pulp from the resinous chips was characterized by favorable length and strength of fibre. There was no appreciable difference between the pulp obtained from the resinous wood direct and that from the chips which had been first extracted with NaOH or Na_2CO_3 . The pulp from the resinous chips was harder to handle, because of the large amount of rosin soap mixed therewith.

The yields of moisture-free pulp varied from 17 to 25 per cent of the weight of the original wood, depending on whether the cooking was carried to the point of soft, light-brown pulp or stopped at the "raw" stage to give stiffer, darker fibre. Such yields would be too low to warrant a simple pulping treatment of the wood, although the figures represent the normal yields of 35-50 per cent on the basis of moisture-free and resin-free wood. The recovery of rosin and turpentine becomes essential in the treatment of rich wood.

II. Practical Experiments.

A series of experiments was next undertaken on a somewhat larger scale to approach a little more closely the conditions which would be met in commercial operation. The aim was to prepare the wood in the form of chips of the ordinary pulping size, then to subject the chips to a mild preliminary steaming in dilute alkali to recover the rosin and turpentine, and finally to cook the extracted chips in stronger alkali in the usual way for pulp. The preliminary extraction was studied to determine the conditions for complete solution of the rosin and simultaneous distillation of the turpentine without too serious an attack of the wood itself. The draining of the alkali extract from the chips and the salting out of the rosin soap by subsequent addition of excess caustic soda were carried out with conservation of alkali in mind, as well as high recovery of rosin soap. The second stage of the process—the production of pulp from the extracted chips—was carried through mainly to note any possible deleterious effect of the preliminary steaming on the quality or yield of the final pulp. The experiments were designed to throw light on the problem of commercial feasibility rather than to establish exact practical data.

The wood studied was limited to box-face slab material. As no pulp-wood chipper was available, the cleaned slabs were reduced to chips by sawing in short lengths of about one inch and splitting as uniformly as possible. Fine material was eliminated and the chips were reduced to an average size of about $1\frac{1}{8}$ in. $\times$ $\frac{3}{4}$ in. $\times$ $\frac{3}{32}$ in., the thickness ($\frac{3}{32}$ in.) being the dimension held most rigidly within narrow limits. These chips were considerably longer than the smallest commercial size, and, as penetration of wood proceeds most readily along the grain, the conditions for alkali extraction were certainly as severe as industrial practice would necessitate. The chips used in Experiment 6 were prepared from the main supply by reducing the size to approximately $1\frac{1}{8}$ in. $\times$ $\frac{1}{4}$ - $\frac{3}{4}$ in. $\times$ $\frac{1}{16}$ in. The main supply of chips was thoroughly mixed and a representative sample obtained for analysis by quartering and subdividing.

Composition of Wood

The rosin content was determined by thoroughly extracting 25 gram portions of the very fine chips with ether in a Soxhlet extractor fitted with ground-glass connections. The rosin was finally dried to constant weight by heating in a Freas electric oven at 105°. Occasional rolling of the flasks hastened the removal of the ether and turpentine. Checks within one or two tenths of a percent were considered satisfactory.

By drying the above chips at 105° after extraction with ether a figure was obtained representing the percentage of "actual wood"—free from moisture, rosin and turpentine. This value has been used in computing the true pulp yields.

To determine the effect on the rosin of extraction by alkali, weighed quantities of the sample chips were heated near the boiling point in dilute caustic soda solution. By repeated decantation and heating with fresh caustic, there was ensured complete saponification of the rosin and thorough washing of the chips. The combined fractions thus obtained were precipitated with acid and the rosin extracted with ether. To minimize the tendency towards emulsification of the humus and to make the operation as simple as possible, the alkaline liquor was placed in a separatory funnel, acidified with HCl or H₂SO₄, and shaken with ether while still slightly warm. The suspension of humus between the water and ether layers prevented complete removal of the lower aqueous layer, although the greater part could be drawn off directly. The clear, upper portion of the ether extract was decanted through a small plug of absorbent cotton into a second separatory funnel. The residual gelatinous humus was then washed several times by decantation with fresh ether and finally filtered on the cotton and washed with solvent. The small quantity of water was then easily removed in the second separatory and the rosin was determined in the usual way. This cycle gave values for rosin which were a few tenths of a percent lower than the direct ether figure. Possible decomposition of gums by the caustic and slight mechanical losses of rosin during

recovery may explain this discrepancy. Previous tests had shown that a trace of humus was dissolved by the ether, but this amount was not enough to appreciably affect the rosin determination.

The alkali-extracted chips, after thorough washing with water, were dried, weighed and extracted with ether. Only a faint trace of resinous material was obtained on evaporation of the ether, showing that the alkali had completely dissolved the rosin. The weight of the extracted chips varied from 45 to 50 per cent of the weight of the original wood, whereas the actual wood content was found to be over 54 per cent, as determined after direct ether extraction of the wood. The discrepancy indicates the extent of lignin decomposition by the alkali.

The percentage of volatile oils could not be accurately determined on a small scale, so the highest yield obtained in the subsequent steaming experiments has been taken as a close approximation of the true "turpentine" content of the wood. In Experiments 5 and 6, 1,500 grams of wood yielded 145 cubic centimeters of turps., weighing approximately 126 grams on the basis of 0.87 specific gravity. (Actual specific gravity—0.8743 at 15°C.) This shows that the wood contained close to 8.4 per cent by weight of volatile oils.

The average composition of the wood supply was found to be as follows:—

Actual wood.....	54.3%
Rosin (by ether).....	32.1%
Volatile oils.....	8.4%
Moisture (by diff.).....	5.2%
	100.0%
Rosin (by NaOH).....	31.8%

Thus the total oleoresin amounted to $32.1 + 8.4 = 40.5$ per cent, made up of 79.2 per cent rosin and 20.8 per cent volatile oils.

Apparatus

The digester used in carrying out the extraction and cooking of the wood was made from an extra-heavy cast iron tee, 6 in. x 6 in. x 4 in. The

apparatus was supported in a horizontal position by resting the flanges in two concrete yokes. The 4 in. outlet of the tee was turned upward to act as a dome for the collection of steam and turpentine vapor; this arm was also used for charging and discharging. The digester was equipped with thermometer pocket, pressure gage, and relief line controlled by a needle valve and leading to a glass condenser. An internal stirring device, consisting of a small shaft fitted with arms, allowed mixing of the contents of the digester when desired. As condensation was too great when the digester was heated by live steam, heat was furnished by two large circular gas burners.

Manipulation

The manipulation was much the same in all the experiments. For the preliminary extraction, from one to two kilograms of resinous chips were placed in the digester and covered with a measured volume of alkaline liquor, containing the desired amount of NaOH or Na_2CO_3 . It was found that considerable space had to be left for steam collection on account of the tendency towards foaming. The top flange was then securely bolted in place, all necessary connections were made and the burners started. In about an hour there was evidence of pressure and the relief line was opened to permit steam distillation of the volatile oils. The burners were controlled to maintain a fixed, low pressure (between 15 and 30 pounds) for extraction of the rosin.

Agitation was carried on continuously or intermittently to prevent local overheating and to facilitate solution of the rosin. Continuous stirring tended to fray the chips and render them less suitable for pulping.

The turpentine fractions were in most cases isolated every fifteen minutes during the relieving period. Curves are given showing the rate of evolution of the volatile oils and the changes in refractive index and specific gravity during the course of distillation for typical experiments.

After the preliminary treatment no longer yielded turpentine in measurable amounts, the burners

were removed and the pressure drawn down. The digester was then inverted by rotating in its seat and the hot liquor drained through the relief line.

The "direct extract" was dark brown in color and the rosin was in perfect solution. For analytical purposes the liquor was aliquoted. This presented some difficulties; the liquor had to be kept hot to prevent precipitation of the rosin soap and the syrupy solution was not easy to handle. Some of the aliquot portions were strengthened while hot with additional caustic soda to make the precipitation of resinate more nearly complete. On cooling, the direct extract gave bulky precipitates of fairly white rosin soap. The dark, supernatant liquors were decanted and drained through cotton or filter paper, and analyzed for unprecipitated rosin. The soap, more or less contaminated with humus and liquor, was dissolved in water and the rosin determined in the usual way.

The chips retained from one to one and a half times their weight of liquor after draining. This represented a serious loss of rosin. In order to recover most of this soap, the chips were washed by covering with hot water and boiling for some time. The "first wash liquor" was drained as before, cooled and aliquoted for determination of rosin content. The color of the solution was dark brown. No soap precipitated on cooling, although about 90 per cent could be precipitated by strengthening moderately with caustic soda.

To further clean the chips enough to allow sampling and careful examination, the wood was washed a second time by boiling with fresh water. This "second wash liquor" contained but little rosin. In actual practice the chips would be ready for the introduction of pulping liquor after draining the first wash liquor from the digester.

The extracted chips after washing as above were discharged from the digester and allowed to dry somewhat. The chips had been appreciably softened by the alkali and darkened by partial attack of the lignin. After thorough mixing, the weight was taken and the mixture sampled. The sample was reduced to small chips and boiled with successive

portions of water to remove the last traces of sodium resinate. This final washing yielded small amounts of rosin soap. The chips were then dried in the oven and extracted with ether to determine the percentage of unsaponified rosin left in the wood. This indicated the efficiency of the alkali extraction.

The sample of chips was finally dried at 105°C. and weighed, giving the percentage of dry, rosin-free wood. The difference between the true wood content of the original resinous material and the weight of the wood after alkali extraction showed the extent of solution of the lignocellulose.

The second stage of the treatment was the production of pulp from the wood. The main portion of the chips, after alkali extraction and washing, was returned to the digester for the soda cook. Caustic soda solution was added to cover the chips and provide amounts of Na_2O varying from 15 to 35 per cent of the weight of the wood.

A gage reading of 100 pounds was reached in 1-1½ hours. The pressure was held at this arbitrary value for about three hours to obtain satisfactory disintegration of the wood. The preliminary treatment had already dissolved some of the lignin, so the final cooking was comparatively short.

The contents of the digester were agitated by stirring frequently. Distillation was carried on at intervals to detect any further evolution of turpentine. Only a few drops were obtained, except in those cases where preliminary extraction of the rosin had been incomplete.

At the end of the cook the pressure was drawn down, the hot liquor drained off and the pulp washed thoroughly. To determine the yield, the pulp was pressed, carefully sampled, and the aliquot portion dried at 105°C.

The pulp was refined in the beater, samples being taken at intervals and made into hand sheets.

Outline of Experiments

Experiment 1 served primarily to standardize the apparatus. 2,000 grams of wood and 7,000 c.c.

of liquor allowed about 1,000 c.c. free space in the dome of the digester for steam collection. This was found to be insufficient, due to surging over of the alkaline liquor. Contamination of the turpentine distillate by alkali and rosin soap not only resulted in a loss of rosin but also caused more or less retention of turpentine in the aqueous layer. The chips were heated with a 3.4 per cent NaOH solution (2.6 per cent Na_2O), the total caustic being 3.2 times the amount theoretically necessary for the saponification of the rosin. A steam pressure of 20 pounds was maintained for 3.5 hours. Although the bulk of the turpentine was removed in the first hour, the fullness of the digester prevented efficient recovery of the least portions in the time allowed. On examination of the chips it was found that considerable rosin still remained unsaponified. In the soda cook a 4.1 per cent NaOH solution was used, providing a ratio of Na_2O to wood of 24 per cent. A pressure of 100 pounds for $2\frac{1}{4}$ hours failed to give proper disintegration of the wood fibre.

In Experiment 2 the digester was filled only about two-thirds full and a very small excess of caustic soda (1.6 times theory) was used. Distillation was carried on at 30-40 pounds in an attempt to hasten the evolution of the turpentine. After two hours the fractions became very small and steaming was discontinued at the end of 3 hours. Conditions for turpentine evolution were particularly favorable on account of the large free space left in the digester and there was no contamination of the distillate. However, the yield of crude turpentine (41.3 gals. per cord) was lower than in subsequent runs and a large proportion of the rosin was left in the chips in the free state. Titration of the liquors showed that the caustic had been completely neutralized during the preliminary extraction, which explained the imperfect penetration of the wood. This pointed to the necessity of employing a larger excess of alkali in order to take care of neutralization by the humic acids formed. The soda cook was carried on with 2.6 per cent caustic solution. The maintenance of

high pressure for 4 hours gave a soft pulp, the yield being 22.5 per cent of the original wood and 41.5 per cent of the actual wood contained therein.

In Experiment 3 the proportion of caustic soda was raised to a little over twice the theoretical amount for saponification and distillation of the turpentine was carried on for 4 hours at 25-30 pounds pressure. Disintegration of the rosin was sufficiently thorough to allow a high recovery of turpentine (44.6 gals, per cord), but an appreciable amount of rosin (7.8 %) remained unsaponified. Analysis of the liquor after extraction showed an absence of excess caustic, indicating that the proper alkali ratio had not yet been reached. The weight of the extracted chips was found to be 44.8 per cent of the original resinous wood, so that the decomposition of the lignin and other non-resinous constituents of the wood had amounted to 9.5 per cent of the original wood or 17.5 per cent of the "actual wood". In this experiment for the first time careful attention was paid to the distribution of the rosin. The direct extract contained 66.2 per cent of the true rosin content in the form of rosin soap. By direct cooling only 72.7 per cent of this soap was precipitated, due to the marked solubility in the faintly alkaline solution. On strengthening the liquor to 8 per cent NaOH, however, 96 per cent of the soap was deposited, representing 63.5 per cent of the total rosin in the wood. The first wash liquor contained 11.7 per cent of the total rosin and the second wash liquor an additional 2.9 per cent. The chips retained 7.8 per cent of the rosin in the free state and about 3 per cent more in the form of soap which had escaped the first two washings. A small amount of soap was found in the aqueous distillate, while the balance (about 7 per cent) represented decomposition by the alkali and slight mechanical losses. Final steaming of the chips in 5.4 per cent NaOH for $3\frac{1}{2}$ hours yielded 41 per cent of soft, thoroughly disintegrated pulp.

To determine the effect of stronger caustic soda, a ratio of 4.34 was used in Experiment 4. Extraction of rosin was in this case complete and the

recovery of the turpentine was accomplished more quickly. A large excess of NaOH remained after extraction and this experiment probably represents the upper limit as far as ratio of alkali to wood is concerned. The direct extract contained 77.2 per cent of the total rosin, 97 per cent of which was precipitated as soap on addition of excess caustic soda. Only 0.15 per cent of the rosin content of the wood remained unsaponified in the chips. The stronger caustic occasioned solution of 24.1 per cent of the actual wood content. The second stage of the process gave a yield of 41.8 per cent pulp, the fibre being softer than desired.

Experiment 5 is undoubtedly the most typical of the series. A lower ratio of Na_2O (3.47) was found to be entirely satisfactory. The main extraction was carried on at the lower pressure of 15 pounds and an examination of the turpentine curve in Figure 2 will show that higher pressures are apparently not necessary in obtaining rapid distillation of the volatile oils. The time under pressure was purposely lengthened to 4 hours and the pressure finally raised to 20 pounds to ensure a maximum yield of turpentine. The percentage calculated from this run has been chosen as representing the true "turpentine" content of the wood. Extraction of rosin was practically complete and considerable excess of caustic was present in the liquors. The direct extract contained 74.5 per cent of the total rosin and the first wash liquor an additional 11.2 per cent.

Special attention is called to the fact that in this experiment the chips were finally cooked according to the procedure suggested for industrial application. The main portion of the direct extract was strengthened with a calculated amount of caustic soda to precipitate the rosin soap more completely. The black supernatant liquor was then used for the soda cook. The pulp so obtained was in no way inferior to the fibres from the other runs. The yield was 46.4 per cent of the actual wood. The pulp retained the general chip form, but was easily disintegrated by hand and after beating was readily made up into uniform sheets of favorable strength and color.

Experiment 6 represents a run on smaller chips to ascertain the differences in alkali penetration. A batch of larger chips from the main supply was reduced by splitting to an average size of about $1\frac{1}{8}$ in. x $\frac{1}{4}$ - $\frac{3}{4}$ in. x $\frac{1}{16}$ in. These chips were about half the thickness of those in the other seven experiments and might be difficult to obtain on an industrial scale without sacrificing uniformity. However, it would be entirely practicable to use chips smaller than those of the main supply and Experiment 6 indicates the general variations with the finer material.

The wood was treated practically the same as in the preceding experiment. The amount of caustic soda was reduced to 3 times that theoretically necessary for saponification and distillation was carried on at the lowest feasible pressure (15-20 pounds). It was found that the last portions of turpentine were removed more readily than with larger chips and the time of preliminary treatment was materially shortened, due to the more rapid penetration of the alkali to the interior of the chips. There was no appreciable difference in extent of lignin decomposition, the loss in weight sustained by the "actual wood" (23.2 per cent) being even less than in Experiment 5 (24.8 per cent) by reason of the shorter steaming period. The soda cook gave a high yield of pulp (47.7 per cent) and the pulp was of excellent quality. Preserving the full length of the chips on reduction of the wood for this experiment no doubt obviated the tendency toward short, uneven fibre from very small chips.

In Experiment 7 an attempt was made to extract the oleoresin by means of sodium carbonate. An ample excess of carbonate was used (3.26 times the saponification value) and the preliminary treatment was executed in a manner which the experience with caustic soda suggested as most favorable to extraction. It was found that penetration of the wood was slow and that solution of the rosin was far from being complete in the reasonably long period allowed for heating. Furthermore, frothing was more troublesome than with caustic

soda and it was difficult to obtain a clear distillate. Distillation of turpentine was slower and the yield was low (41 gals. per cord), due to retention of volatile oil by the unsaponified rosin remaining in the chips. This was apparent from the recovery of an additional 2.9 gals. per cord during the soda cook. A decided advantage was noticed, however, in the decreased attack of the lignocellulose by the weaker alkali, the amount dissolved being only 11.4 per cent of the actual wood. The chips were finally cooked in a 2.3 per cent caustic soda solution, and kept at 100 pounds pressure for $2\frac{3}{4}$ hours. Disintegration was hardly thorough enough, as the pulp retained the chip form and required long treatment in the beater before the fibres would felt properly. This explains the high yield of 49.7 per cent.

In Experiment 8 the resinous chips were submitted to a single treatment for pulp to provide a standard for the comparison of fibres. A 4.8 per cent solution of NaOH was used, containing an amount of Na_2O equal to 18.5 per cent of the weight of the resinous wood. With the intention of also making this run a quantitative determination of turpentine the pressure was first held at about 30 pounds for 3 hours in order to distil over the turpentine at a moderate temperature. Unfortunately, a slight leak developed in the top of the digester and the recovery of volatile oils amounted to only 32.6 gals. per cord. After most of the turpentine had been removed, the pressure was raised to 100 pounds and cooking was continued for 3 hours more. The yield of pulp was 44.2 per cent and the fibre was long and uniform, although apparently no different from the pulp obtained in certain of the two-stage operations.

TABLE I

Preliminary Alkali Extraction of Resinous Chips

	Experiment Number.						
	1	2	3	4	5	6*	7
Kind of Alkali Used....	NaOH	NaOH	NaOH	NaOH	NaOH	NaOH	Na ₂ CO ₃
Wt. of Resinous Chips—Grams.....	2000	1000	1000	1500	1500	1500	1500
Na ₂ O Used—Multiple of Theoretical Value.	3.2	1.6	2.17	4.34	3.47	3.0	3.26
Volume of Liquor—c.c.	7000	6000	5000	7000	7000	7150	7000
Strength of Liquor—% Na ₂ O.....	2.6	0.77	1.25	2.68	2.14	1.82	2.02
Relieving Pressure—Pounds Gage.....	20	30-40	25-30	25	15-20	15-20	30
Time under Pressure—Hours.....	3.5	3	4	3.75	4	3.5	3.5
Crude Turpentine—c.c.	113	86	93	139	145	145	128
Crude Turpentine—Gals. per Cord.....	27.1	41.3	44.6	44.5	46.4	46.4	41.0
Crude Turpentine—Index of Refraction at 15°C.....	..	1.4742	1.4742	1.4738	1.4741	1.4733	1.4742
Crude Turpentine—Specific Gravity at 15°C.....	..	0.8753	0.8854	0.8849	0.8743	0.8770	0.8774
Dry, Extracted Chips (Rosin-free)—% of Original Wood.	..	..	44.8	41.2	40.8	41.7	48.1
"Humus," Dissolved—% of Actual Wood.....	..	..	17.5	24.1	24.8	23.2	11.4

*Extraction of Smaller Chips.

Discussion of Table I

Table 1 contains most of the important data bearing on the preliminary extractions. The rosin determinations have been reserved for later discussion (see Table 2.)

In computing turpentine yield, a factor was worked out for the transformation of volume in cubic centimeters to gallons per cord. A yield of 1 c.c. from 100 grams of wood is equivalent to a production of $\frac{4,000}{100 \times 8.335} = 4.8$ gallons from a cord of 4,000 pounds. The wood used probably weighed considerably more than 4,000 pounds per cord, but this figure has been chosen as a conservative estimate for rich pine.

The index of refraction was obtained by the use of a Pulfrich refractometer. The readings were made at room temperatures (17-23°C.) and the index at 15°C. calculated. The positive correction of 0.00047 per degree centigrade was used, in accordance with the recommendation of the govern-

ment laboratories. (U. S. Dept. Agr., Forest Service, Bul. 105, p. 13.)

Specific gravity was in all cases measured at 15°C. by the use of cooling baths.

The important variable in the various runs was the ratio of alkali to wood. The unit basis for calculating the amount of NaOH or Na₂CO₃ to be used in the preliminary treatment was the weight of Na₂O theoretically necessary to saponify the rosin in the wood. The average combining weight of American rosins has been placed by Lewkowitsch ("Chemical Technology and Analysis of Oils, Fats and Waxes," Vol. 1, p. 499) at 346, and for convenience this figure has been taken as an approximation of the combining weight of the rosin in the chips under consideration. On this basis rosin would require $31/346 = 8.96$ per cent of its weight of Na₂O to produce a neutral sodium resinate. The wood under consideration contained 32.1 per cent of rosin, so that 100 parts of resinous wood required at least 2.88 parts of Na₂O for complete saponification of the rosin therein. The amounts of Na₂O actually used have been expressed as multiples of this unit value. The attempt was to find the least amount of caustic which would completely extract the rosin before neutralization of alkali by the rosin and humic acids, under conditions allowing efficient turpentine distillation and still preventing undue attack of the wood itself. With the preliminary extraction continued for 3.5-4 hours at 15-30 pounds pressure, the lower limit for NaOH was found to lie somewhere between 2.17 (Expt. 3) and 3.0 (Expt. 6) times the theoretical amount of caustic. Under the conditions employed, the minimum amount of caustic necessary for extraction could be safely placed at about 2.5 times the theoretical value. The excess above that needed for saponification of the rosin was of course neutralized by combining with the decomposition products from the wood itself.

The relieving pressure was varied somewhat, but without appreciable change in the other steaming factors. The aim was to discover the lowest pres-

sure at which distillation of turpentine and penetration of the wood could be carried on without unduly lengthening the time of treatment. A pressure of 15-20 pounds was found to be effective in achieving the most favorable results.

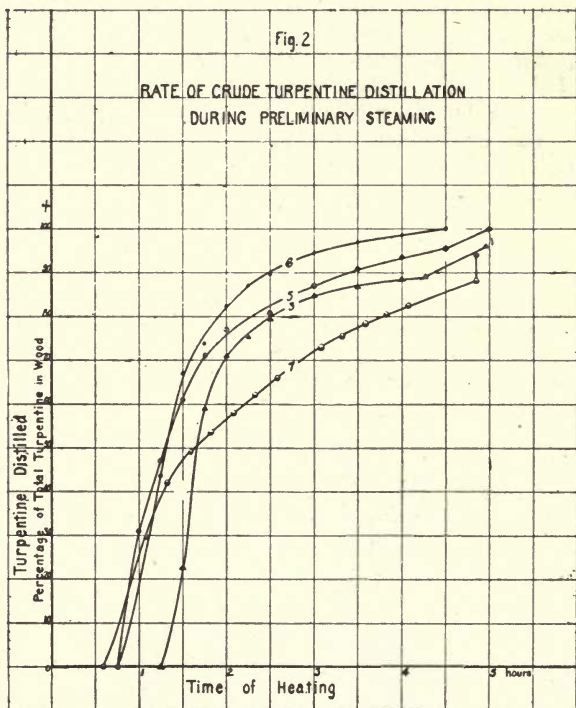
The time consumed in extraction varied from 3.5 to 4 hours and must in most cases be considered a maximum, because of the attempt to recover all the turpentine. The greater proportion of the run was spent in distilling the last small portions of oil. An important feature in the design of a digester for practical operation would be the provision for rapid steam distillation, so that the final portions of volatile oil could be carried over as soon as liberated by disintegration of the rosin. This would shorten the time of preliminary treatment and decrease the effect of the alkali on the rosin and the wood. A large dome or distilling head set with closed steam coils might successfully break the froth and allow proper control of distillation from the digester.

There was considerable attack of the lignocellulose, as may be seen from the amounts of humus, etc., dissolved (11.4—24.8 per cent of the actual wood). This decomposition of lignin seemed to depend as much on the time of contact with the alkali as on the ratio of caustic used. This action does not signify a waste of alkali or an injury to the wood, but rather represents the first stages of the ordinary pulping operation. The dissolving of the humus is objectionable only because of its contamination of the rosin soap and because of the extra steps involved in removing it from the same.

Rate of Turpentine Distillation

Representative curves showing the rates of turpentine distillation are given in Figure 2. In order to compare the results on a convenient basis the yields from Expts. 5 and 6 have been taken as standard and assumed to be 100 per cent of the volatile oils in the wood. All turpentine fractions in the four experiments considered have been calculated as percentages of this maximum value. The

abscissas represent the total time of heating, starting from room temperature. The ordinates show the percentages of the total turpentine in the wood, which were recovered at different stages of the steaming.



The most noticeable feature is that the great bulk of the turpentine was recovered during the first stages of relieving and about as fast as the steam could carry it over. After relieving one hour, approximately 75 per cent of the turpentine had been recovered. The last 25 per cent was evolved more slowly. With proper appliances for more rapid distillation of steam, it is quite probable that this proportion of the turpentine could be recovered in much less time. The final upward turns of the curves represent the last fractions which were carried over by the rather large quantities of steam

drawn off in reducing the pressure to atmosphere. The curve for Expt. 7 shows the retardation when sodium carbonate was used. The extraction of rosin was in this case incomplete. The vertical portion of this curve indicates the turpentine fraction recovered during final cooking for pulp.

Another outstanding feature is the remarkable similarity of the curves, in spite of the differences in treating the wood. In the three experiments where caustic soda was used it will be seen that the curves almost converge at the two hour mark. This indicates that it makes little difference whether distillation is commenced as soon as pressure is evidenced or whether relieving is postponed a little.

The gradual flattening of all the curves and the marked retardation in turpentine evolution in Expt. 7, where solution of the rosin was slow and incomplete, indicate pretty clearly that disintegration of the rosin is necessary for efficient turpentine recovery. This is the difficulty experienced in the ordinary steam distillation process, where the fine resinous material must be subjected to the action of steam for 3-10 hours and even then without the recovery of the last traces of oil. In a degree, then, the curves represent the speed of alkali penetration of the wood. Evidently, an important phase of the distillation is to ensure rapid removal of the turpentine from the digester during the last stages of the steaming period, so that the operation can be discontinued as soon as the rosin is dissolved and the last of the oil thereby liberated.

The amounts of steam necessary to carry over the various turpentine fractions are important from a practical view-point. In nearly all cases the first 50 per cent of the oil was distilled with less than its own volume of condensed water-vapor. The next 25 per cent required from 1 to 4 times its volume of aqueous distillate, the ratios in the most representative experiments (4, 5 and 6) being 1.2, 1.3, and 1.0 respectively. The fraction from 75 to 90 per cent required ratios of from 7 to 10 under properly regulated conditions. The figures for the final 10 per cent are not significant, because of the large amount of steam removed at

the end of the treatment to ensure evolution of the last traces of turpentine. The ratios for this period varied from 40 to 50. It will be apparent that the ratios of condensed water vapor to turpentine are well within the practical limits. In fact, a much more rapid evolution of steam would be justified in order to shorten the steaming period.

The nature of the turpentine curves suggests that it might be found more economical in practice to discontinue the preliminary steaming before the last traces of turpentine were removed. This would mean a saving in steam consumption and a less severe attack of the wood itself.

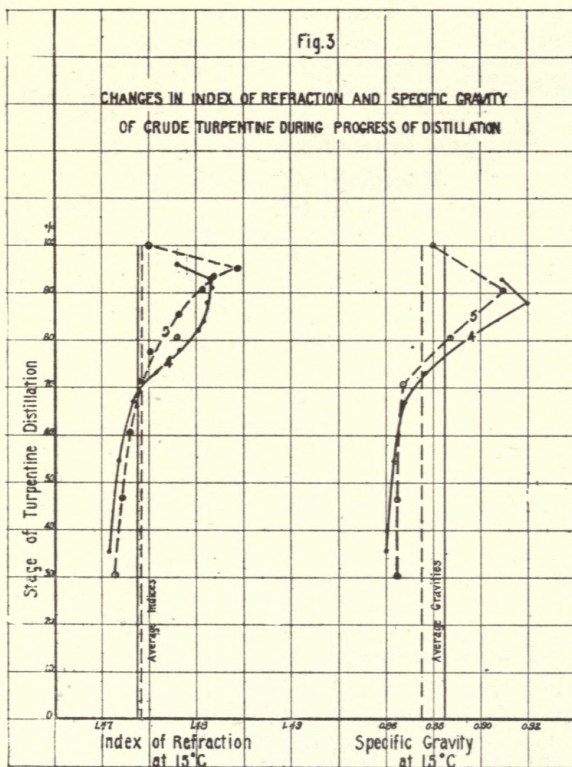
In conclusion it seems reasonable to assume that a properly conducted alkali extraction will allow recovery of all the volatile oils in the wood in a high state of purity.

Partial Fractionation of Volatile Oils

Figure 3 will serve to show certain changes in the nature of the volatile oils during the progress of distillation. The fractions were saved separately every fifteen minutes in Experiments 4 and 5 and the refractive index and specific gravity constants of each fraction were determined. The ordinates have been chosen to represent the various stages of turpentine distillation, expressed in percentages of the total turpentine content of the wood. The backward turn at the end of each curve is occasioned by the final fraction obtained while drawing down the pressure. The average constants, obtained by finally combining all the fractions, are shown by the vertical lines.

The curves of index of refraction and specific gravity for a single experiment follow closely parallel to one another. Moreover, the curves are materially the same for the two experiments. It is apparent that the oil became heavier as distillation proceeded and that the last period of steaming was spent in removing the fractions which approach pine oil in general properties. This shows that distillation of the crude turpentine is not coincident with its liberation from the rosin, for otherwise the

distillate would be uniform throughout the run. The heavier constituents are carried over more slowly by the steam and require extended treatment to ensure their recovery. This also points to the advantage of rapid steam evolution during the last stages of the preliminary treatment in order to remove the heavier oils from the solution as quickly as possible.



The change in the nature of the oil during distillation suggests that this direct recovery might be used as a preliminary fractionation of the crude turpentine into "wood turpentine" and "pine oil."

TABLE 2

Distribution of Rosin after Alkali Extraction

[Results expressed in Percentages of Total Rosin in Original Wood—Ether Extract = 32.1 per cent.]

Fraction.	Form of Rosin.	3	Experiment 4	5	Number 6*	7°
Direct Extract—Direct Cooling						
	Soap Ppt.....	48.2	70.7	65.5	59.2	53.3
	Filtrate.....	18.0	5.9	8.7	20.2	8.4
Direct Extract—Strengthening to 6 to 8% NaOH						
	Soap Ppt.....	63.5	75.0	72.0	76.5	59.4
	Filtrate.....	2.7	2.8	2.8	2.8	2.3
Direct Extract—Total Rosin as Soap		66.2	77.2	74.5	79.4	61.7
1st Wash Liquor.. Sol. Rosin Soap...		11.7	10.6	11.2	9.7	10.0
2nd Wash Liquor.. Sol. Rosin Soap...		2.9	3.4	2.5	2.9	4.4
Washed Chips.. Unsaponified Rosin..		7.8	0.15	0.9	0.14	8.0
Balance.....		11.4	8.6	10.9	7.9	15.9

* Extraction of Smaller Chips with NaOH.

° Extraction of Larger Chips with Na₂CO₃.

Reclaiming of Rosin

Table 2 shows the distribution of the rosin content of the wood after alkali extraction and washing. The analytical results have been expressed as percentages of the total rosin in the original wood as determined by extraction with ether.

As already mentioned, the direct extract was aliquoted and treated in two ways. Some portions were allowed to cool directly; others were treated with additional caustic soda to precipitate the soap more completely and leave a supernatant liquor, which would represent a solution available for the final soda cook in industrial practice. Where solution of the rosin was complete, from 75 to 79 per cent was removed in the first draining. Of this amount from 96 to 97 per cent was recovered in the form of soap precipitate by strengthening the liquor with caustic soda to from 6 to 8 per cent. The sodium resinate remaining in solution was of course dependent on the solubility of the soap in the strong alkali, and on this account was practically a constant quantity—2.3 to 2.8 per cent of the total. The percentage would be relatively higher in the case of leaner woods, but the actual loss is comparatively small. This unrecovered rosin would be carried through the soda cook and would be of some advantage as fuel in the final incineration involved in the recovery of alkali from the waste pulping liquors.

The figures for direct cooling of the extract are interesting only in showing the necessity of salting out the soap with stronger caustic. The filtrate losses were high and varied inversely as the excess of alkali left in the extract after preliminary steaming. In Expt. 6, for instance, where the caustic was nearly all neutralized, the rosin remaining in solution amounted to 20.2 per cent. of the total.

From 10 to 12 per cent of the rosin was removed in the first washing of the chips. This treatment must therefore be looked upon as an important step in the process. It was found that 80 or 90 per cent of this rosin soap could be recovered by precipitation with caustic. An industrial cycle might involve the salting out of the resinate in this way. An alternative would be the addition of enough caustic soda to the first wash liquor to allow its use directly as the alkali liquor for extraction of the wood in the succeeding cycle. This would permit the precipitation of the inherent resinate in the next "direct extract."

From the direct extract and the first wash liquor it was possible to recover about 85 per cent of the total rosin in the wood in the form of rosin soap precipitate, salted out of solution by means of caustic soda.

Comparatively little rosin was obtained from the second wash liquor and this step would hardly be justified in practice.

The unsaponified rosin, determined by ether extraction of the washed, dried chips, indicates the efficiency of the alkali extraction. In Expt. 3, 7.8 per cent of the rosin was left undissolved by reason of the premature neutralization of the small amount of caustic used. In Expt. 7 the sodium carbonate failed to penetrate the wood in the time allowed for steaming and 8 per cent of the rosin was retained in the free state by the chips. Experiments 4, 5 and 6 represent practically perfect extractions of rosin.

The "balance" includes 3-5 per cent of soluble resinate retained by the chips after the two washings and small quantities of soapy liquor surging

over with the distillate during steaming. Mechanical losses in handling the liquors and in analysis are also involved in this figure. The main discrepancy seems to be due to decomposition occasioned by the alkali in dissolving the more or less complex resinous content of the wood.

TABLE 3
Soda Cooks for Pulp

	Experiment Number.							
	1	2	3	4	5*	6°	7	8x
Ratio of Liquor to Wood..	7.5	14.0	6.7	13.5	8.16	9.6	10.0	5.0
Ratio of Na ₂ O to Wood-%	24	28	27.9	35.0	19.8	16.5	18.1	18.5
Strength of Alk. Liquor—								
% Na ₂ O.....	3.2	2.0	4.17	2.6	2.42	1.72	1.8	3.7
Causticity of Alkali-%....	...	...	94.3	94.8	81.0	94.5	96.0	94.5
Time at 100 Pounds								
Pressure—Hours.....	2.25	4.0	3.5	3.25	2.75	2.5	2.75	3.0
Turp. Recovered—								
Gals. per Cord.....	2.0	0	0.3	0	0	0	2.9	32.6
Yield of Pulp on Dry Basis								
—% of Resinous Wood	...	22.5	22.3	22.8	25.2	25.9	27.0	24.0
Yield of Pulp on Dry Basis								
—% of Actual Wood	...	41.5	41.0	41.8	46.4	47.7	49.7	44.2

*Black Liquor from Preliminary Extraction used as Cooking Solution

°Soda Cook on Smaller Chips.

xDirect Soda Cook of Resinous Chips.

Production of Pulp

The more pertinent data on the soda cooks have been assembled in Table 3. For the sake of convenience, caustic soda was used in reducing the wood to pulp. In Expt. 5 the solution used for cooking was the black liquor from the preliminary extraction of rosin, which had been strengthened with caustic soda to salt out most of the resinate. The sulphate process would have yielded better fibre, but in these investigations there seemed no necessity of complicating the treatment by the addition of sodium sulphide.

In the first seven experiments, the chips which had been subjected to alkali extraction and washing were used as raw material. In Expt. 8 a single steaming of the wood was employed. The pressure was held at about 30 pounds for 3 hours in order to disintegrate the rosin and to distil the turpentine without decomposition thereof. The pressure was then raised to 100 pounds for final pulping.

The first two ratios—liquor/ wood and Na₂O/ wood—are based on the dry weight of the extracted

chips in Expts. 1-7, and on the weight of the original resinous wood in Expt. 8.

"Causticity" refers to the ratio of the sodium oxide present in the cooking liquor in the form of NaOH over the total amount present both as NaOH and Na_2CO_3 .

The pulp was dried at 105°C . and the yield calculated first as percentage of the original resinous wood to show the over-all yield, and second as percentage of actual dry rosin-free wood in the original material, to indicate the true efficiency of the pulping operation.

The turpentine figures refer in the first 7 experiments to the additional recovery during the soda cook, signifying in several cases incomplete disintegration of the oleoresin in the preliminary treatment. In Expt. 8 the turpentine was obtained by a combined extraction and pulping of the wood.

The actual data are in many ways not comparable with those in ordinary soda-mill practice. The "liquor/wood" ratio is usually from 4 to 6, when a digester is filled with chips and flooded with liquor. Because of the decreased volume of the wood after preliminary extraction, a larger ratio of cooking solution was necessary to properly fill the experimental digester and prevent exposure of the chips. With lean woods the " Na_2O /wood" is usually from 17 to 25 per cent and the actual consumption of NaOH about 20 per cent, equivalent to about 15 per cent of Na_2O . By reason of the partial attack of the lignin in the preliminary extraction, a ratio of sodium oxide below 20 per cent was found to be most satisfactory. The above considerations necessitated a low strength of cooking liquor—lower than would be necessary in practice. A concentration of 5-10 per cent NaOH is usually employed in practice.

The pressures used in soda cooking vary from 75 to 150 pounds, the higher values applying particularly to deciduous woods, such as poplar and basswood. In these experiments a pressure of 100 pounds was chosen as a satisfactory figure for pine. The time necessary to reduce the pine to pulp was comparatively short due to partial de-

composition during preliminary steaming and also to the more effective action in the small digester.

The outstanding feature of the several experiments was that there was no failure in obtaining strong, long-fibred pulp of good quality. The preliminary extraction did not detract to any noticeable degree from the quality of the final fibre. The soundness of the raw material and the use of large chips was of course largely responsible for the favorable nature of the pulp. In Expts. 2, 3, 4 and 8 the pulp was quite thoroughly disintegrated by the stirring device and the fibre was "soft." It will be seen that low yield is coincident with soft fibre. In Expt. 5 the pulp retained the chip form but yielded to disintegration on handling. Expt. 6 gave a strong pulp from the smaller chips. Expt. 7 represents a "raw" cook, in which the pulp was blown in the form of firm chips. Careful reduction in the beater gave a fibre of dark brown color and considerable strength, although the insufficient cooking had left the fibre somewhat "woody."

The over-all yield of approximately 25 per cent of pulp illustrates the practical drawback in treating this resinous material directly for pulp alone, not to mention the high consumption of alkali which would be involved in dissolving the rosin and the mechanical difficulties in cooking and washing. The true pulp yields are well within the range of ordinary practice. The figures between 45 and 50 per cent must be considered as most typical, inasmuch as the raw material is especially adapted to the production of somewhat raw, strong fibre for making high-grade wrapping papers, etc.

Nature of Products

(1) **Turpentine** : As regards the character of the crude turpentine obtained during alkali extraction, it is apparent that the product represents the volatile oils of the wood practically unchanged by distillation from dilute alkali at low steam pressures. In the refining of the crude turps. from the "Steam Distillation" process, it is customary to redistil after the addition of dilute alkali. It may be said, then, that the volatile oils from the alkali extrac-

tion process have already undergone the first step in refining.

The direct product was in every case clear and only faintly yellowish in color. The oil was without the objectionable odor of "Destructive Distillation" turpentine. The odor was pleasant and of an "essential oil" character, rather than of pure turpentine. This may be ascribed to the pine oil content.

It was not considered necessary to give particular attention to the refining of the crude turpentine. The methods have been carefully worked out and there are no special difficulties involved. (see U. S. Dept. Agric., Forest Service Bull. 105 and Bur. Chem. Bull. 159). Separation into "wood turpentine" and "pine oil" would be accomplished by redistilling with steam, preferably in a column still. The final yield of turpentine, boiling between 155 and 185°C., can be placed at 70-85 per cent, the balance being pine oil boiling above 185°. The turpentine fraction would undoubtedly contain a small quantity of dipentene as impurity, although this amount should be smaller than by direct steam distillation of the wood, where the higher temperatures cause partial decomposition of the oils into dipentene. Pine oil is almost as valuable as turpentine, so that there would be very little waste in purifying the original crude oil.

(2) **Rosin Soap:** The proposed scheme provides for the recovery of rosin from the direct extract and first wash liquor by salting out the rosin soap with caustic soda. It has been shown that 75-85 per cent of the rosin can be obtained in this way from rich wood. The soap precipitates were soft, and more or less contaminated with material derived from the wood itself. Purification from the humus was accomplished by reprecipitations with caustic soda. The soft soap was not successfully filtered and pressed, and for this reason retained appreciable amounts of alkali liquor.

It would seem logical to use the soap as such, without acidifying to liberate free rosin. Rosin soap has marked detergent properties and is a constituent of many commercial soaps. The soap

maker, however, usually incorporates the rosin by neutralizing the excess of free alkali with the free rosin acids, after saponification of the fats. Rosin soap is also used in many lubricating greases.

One of the most reasonable applications is to be found in a paper mill itself. All ordinary papers are sized with rosin, added to the beaters in the form of soap solution and finally precipitated by alum. By dissolving the soap precipitates obtained in the process under discussion, and heating with a certain amount of free rosin, it should not be difficult to provide an emulsion of the composition demanded by the paper maker.

There are possible drawbacks in a scheme of this kind. The presence of oils in size sometimes results in spotting of the finished paper. However, by careful distillation of the crude turpentine during extraction of the wood, it is doubtful if more than a trace of oily matter would find its way into the finished size. The humus carried down by the colloidal sodium resinate detracts somewhat from the white color of the rosin soap and gives a brownish color to the solutions. It is a question whether the small proportion of humus in the original rosin soap would appreciably affect the value of the directly prepared size, except for use on white papers. Humic salts have even been suggested as possible sizing agents in themselves. (E. Rinman, *Svensk Kemiisk Tidskrift*, see *J. Soc. Chem. Ind.*, Feb. 29, 1912, p. 183). At any rate, reprecipitation with caustic soda offers a convenient method of purification.

(3) **Paper Pulp**: In addition to the products mentioned above, it has been shown that the normal yield of high-grade pulp can be obtained from resinous pine by the methods described. The whole process, in fact, has been designed with this end in view. The two-stage treatment adapts itself to the employment of any of the so-called "alkaline" processes for final production of fibre. It would not be desirable to use "sulphate" liquor for extraction of the rosin, but in a sulphate mill, where the two-stage treatment of rich wood was carried on in conjunction with ordinary pulping operations

on lean wood, there should be no difficulty in providing for the preliminary extraction of the rich wood with caustic soda alone. As a source of alkali for cooking, the strengthened black liquor from the "direct extract" was found to be satisfactory.

The pulp obtained from long-leaf pine is characterized by unusual length of fibre, the length being 4-6 millimeters, or about twice that of spruce fibre. This quality, coupled with the favorable strength and flexibility of the fibre, imparts to the finished paper unusual toughness and resistance to folding and bursting.

The soda cooks gave brown pulp, which did not lend itself readily to bleaching. The consumption of bleach was high and the final color was distinctly yellowish. As has already been mentioned, the sulphate process is preferable where bleached pulp is desired.

The pulp from long-leaf pine is well suited for making high-grade wrapping paper, board stock, etc. With further study of the methods for cooking, beating and bleaching, it is expected that the uses of the pulp will be greatly extended.

Significance of Results

The data obtained in these investigations are not necessarily exactly representative of those which would hold in industrial practice. The prime deduction from the experimental results is the feasibility of a two-stage treatment for the chemical utilization of waste southern pine rich in rosin and turpentine. It was possible to obtain a high recovery of valuable products from the primary constituents of the wood. The crude products were isolated in a favorable state of purity and required little subsequent refining. The process was characterized by simplicity in manipulation and in separation of end products. Moreover, the materials used in the reduction, as well as the ultimate products themselves, were few in number and simple in nature.

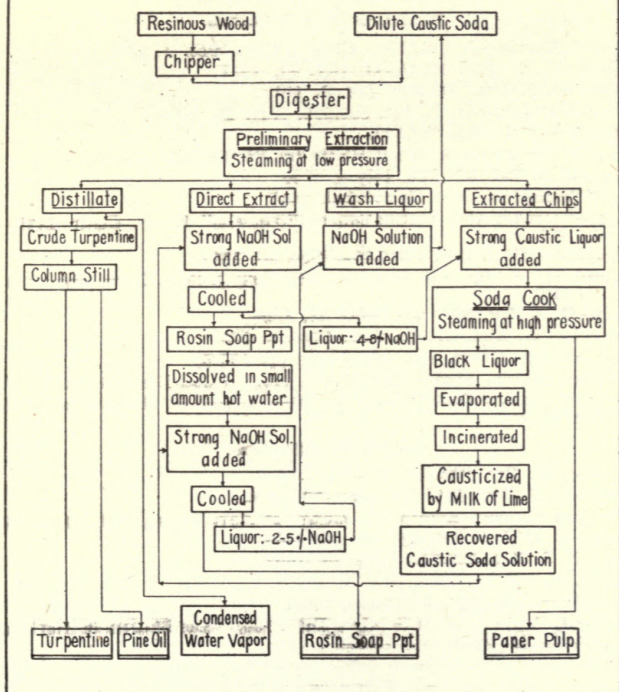
There was no waste of alkali at any point. The portion withdrawn from the cycle in the form of precipitated sodium resinate served to enhance the

value of the rosin fraction. Incineration of the waste pulping liquor provides for the recovery of the balance of the alkali, within the practical limits of mechanical efficiency.

As mentioned before, practical application of this treatment of the more resinous materials could be carried on most conveniently as a supplement to ordinary pulp-mill operations on lean wood. Only slight modifications in certain of the existing digester units would be necessary to take care of the richer grades of pine. The supply of fat wood could be obtained by sorting the raw material received at the pulp mill or by procuring lightwood, etc., from independent sources.

There is also a possibility that the first stage of the process, namely that of extraction with caustic soda or sodium carbonate, could be employed in treating those grades of resinous waste which would not lend themselves to final pulping. Charred or unsound wood might be steamed with dilute alkali for the recovery of rosin and turpentine, without provision for treatment of the extracted chips. The economic merits of such a scheme could be decided only by actual trial.

PROCESS DIAGRAM



ADDITIONAL REFERENCES

Turpentine Orchardng

- Briggs—Chem. World, through Paper, Nov. 13, 1912, p. 21.
French & Withrow—J. Ind. Eng. Chem., 1914, p. 148.
Herty—J. Elisha Mitchell Soc., 23, No. 1, 1907.
U. S. Dept. Agric., Forest Service Bulletins 40, 90, 101, 116, 119;
Circular 34.
Walker—J. Soc. Chem. Ind., 1911, p. 934.

Destructive Distillation

- Benson & Darrin—J. Ind. Eng. Chem., Nov. 1913, p. 935.
Dungan—U. S. Pat. 1,007,341, Oct. 31, 1911.
Gautier—U. S. Pat. 980,509, Jan. 3, 1911.
Gautier & Burger—U. S. Pat. 896,292, Aug. 18, 1908.
Hammatt—U. S. Pat. 843,599.
Harper—"Utilization of Wood Waste by Distillation" (1909).
Jewett—U. S. Pat. 824,872, July 3, 1906.
Klar—"Technologie der Holzverkohlung"
Klason—"Des tructive Distillation of Pine, etc." Chem. Centr. 1909, 1
p. 109.
McLaughlin—U. S. Pat. 1,012,684, Dec. 26, 1911.
Pritchard—U. S. Pat. 880,466, Feb. 25, 1908; J. Soc. Chem. Ind., 1912,
p. 418.
Snyder—U. S. Pat. 821, 264, May 22, 1906.
Teepie—J. Ind. Eng. Chem., Aug. 1913, p. 680.
Walker—J. Am. Chem. Soc. 28, (1906), pp. 103-5.
U. S. Dept. Agric., Forest Service Cir. 114, "Wood Distillation."
U. S. Dept. Agric., Bur. Chem. Cir. 36—"Chemical Methods of Utiliz-
ing Wood."

Steam Distillation

- Danner—U. S. Pat. 883,091, Mar. 24, 1908
Gardner—U. S. Pat. 881, 787, Mar. 10, 1908.
Hawley and Palmer—Eighth Int. Cong. of App. Chem., Vol. 13, p. 151.
Jackson—U. S. Pat. 832,976, Oct. 8, 1906.
Jewett—U. S. Pat. 863,718, Aug. 20, 1907.
Pride—U. S. Pat. 840,955, Jan. 8, 1907.
Rasche—U. S. Pat. 850,098, Ap. 9, 1907.
U. S. Dept. Agric., Forest Service, Bull. 109, "Distillation of Resinous
Woods by Saturated Steam."
Williams—U. S. Pat. 799,426, Sept. 12, 1905.

Extraction Processes

- Bashlin—U. S. Pat. 1,059,261, Ap. 25, 1913.
Craighill—U. S. Pat. 783,367, Feb. 21, 1905.
Frankforter—J. Am. Chem. Soc. 28, (1906), p. 1467.
J. Ind. Eng. Chem. 3, p. 4.
U. S. Pats. 918,989; 918,990, April 20, 1909.
Huggins—U. S. Pat. 1,022,194, April 2, 1912.
Ogilvie, Manningtree & Mitchell—Eng. Pat. 5,978, Mar. 12, 1909.
Rowley—U. S. Pats. 942,106; 942,207, Dec. 7, 1909.
Saylor—U. S. Pat. 945,612, Jan. 4, 1910.

Library of Additional References—Continued

Bath Processes

- Dungan—U. S. Pat. 878,785, Feb. 11, 1908.
 McKenzie—U. S. Pats. 851,687 and 852,236, April 30, 1907; 13,456, Aug. 6, 1912.
 Pope—U. S. Pats. 852,078, April 30, 1907; 959,599, May 31, 1910; 982,631, Jan. 24, 1911; 1,030,011, June 18, 1912.
 Thompson—U. S. Pat. 862,680, Aug. 6, 1907.
 Weed—U. S. Pat. 804,358, Nov. 14, 1905; 805,174, Nov. 21, 1905.

Hydrolysis

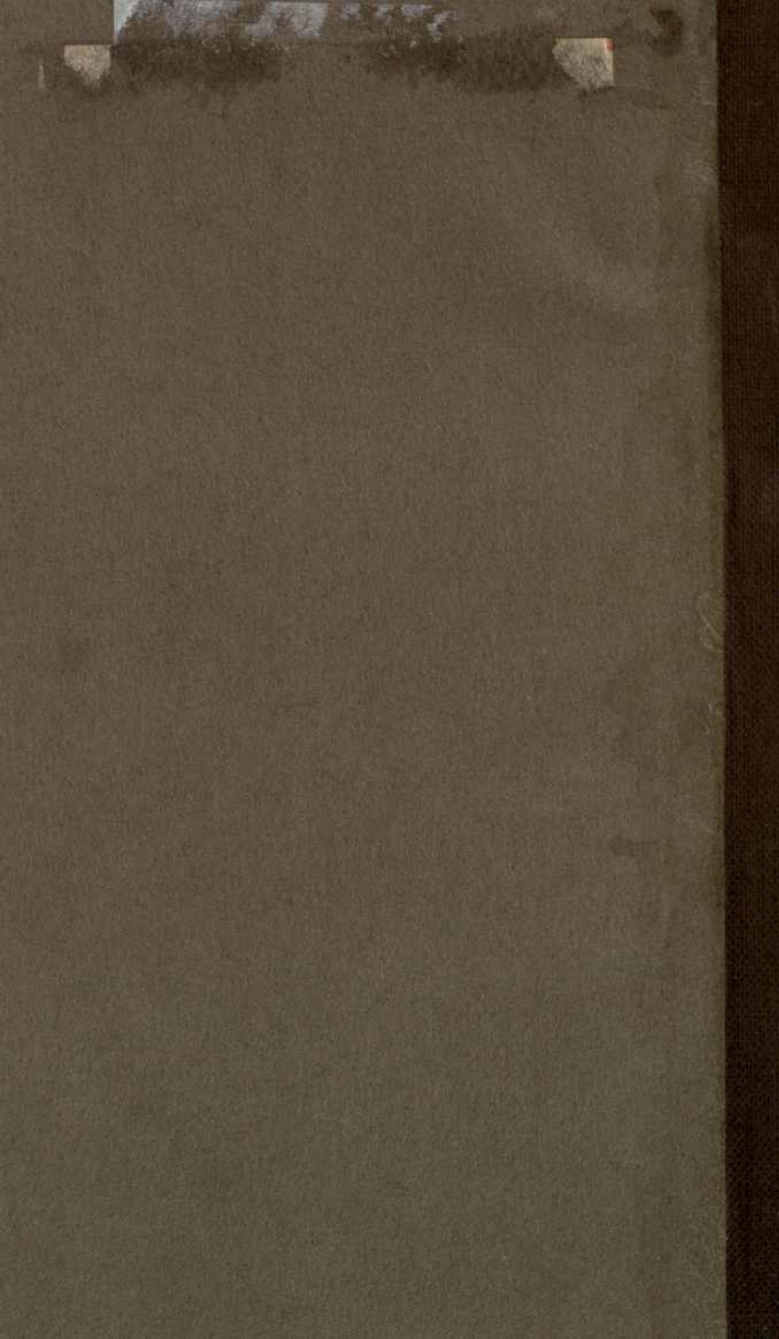
- Borde—"Manufacture of Alcohol from Sawdust," Chem. Eng., June 1910
 Classen—Eng. Pats. 258; 4,199; 12,588, etc.
 Cline—"A possible Utilization of Yellow Pine Stumpage." Am. Lumberman, Feb. 10, 1912, p. 47.
 Cohoe—J. Soc. Chem. Ind. 31, p. 513; U. S. Pats. 985,725-6.
 d'Orlowsky—French Pat. 405,187, July 1909.
 Doughty—U. S. Pat. 930,274, Aug. 3, 1909.
 Ewen and Tomlinson—U. S. Pat. 938,308.
 Gallagher and Pearl—Eighth Int. Cong. of Applied Chem., Vol. 13, p. 147.
 Hirsch—J. Ind. Eng. Chem., July 1912, P. 478.
 J. Newman—"Critical Studies on Hydrolysis of Cellulose and of Wood." (German.)
 Ost and Wilkening—Chem. Ztg. 1910.
 Posnansky and Spassky—Hungarian Pat. 3,716, April 1, 1913.
 Ruttan—J. Soc. Chem. Ind., Dec. 31st, 1909, p. 1290.
 Simonsen—Z. Angew. Chemie, 1898, pp. 962-6 and 1007-1012: 1899 pp. 195-6 and 219-228.
 Tomlinson—U. S. Pats. 1,032,440 to 1,032,450.
 Voerkelius—Wochenblatt fur Papierfabrikation, 1911, 10, p. 852.

Paper Pulp

- Aktschourine—French Pat. 433,424, Aug. 11, 1911.
 German Pat. 248,275, July 12, 1912.
 Hough—U. S. Pats. 931,608, Aug. 17, 1909; 945,394, Jan. 4, 1910; 949,324, Feb. 15, 1910.
 Klason—"Beitrage zur Kenntniss der Chemischen Zusammensetzung des Fichtenholzes," (Berlin, 1911).
 Klason and Segerfelt—Papierfabrikant, 1911, 9, p. 1093 (see J. Soc. Chem. Ind., 1911, p. 1154).
 Rosenblum, Brech and Tyborowski—German Pat. 252,322, Oct. 15, 1912
 Stanley—U. S. Pat. 968,278, Aug. 23, 1910.
 Weiberg—U. S. Pat. 981,042, Jan. 10, 1911
 Williamson—U. S. Pat. 1,025,356, May 7, 1912.
 U. S. Dept. Agric., Forest Service Bull. 123, "Bibliography of the Pulp and Paper Industries."
 U. S. Dept. Agric., Bur. Chem., Cir. 41, "Paper-making Materials and their Conservation."
 Wells—U. S. Dept. Agric., Forest Service, Paper before Am. Chem. Soc., Rochester, Sept. 1913, see P. & P. Mag., Can., Sept. 15, 1913, 629.

BIOGRAPHICAL

John Seaman Bates was born at Woodstock, Ontario, on June 9th, 1888. He entered Acadia University, Wolfville, N.S., in the fall of 1904, and was graduated with the degree of Bachelor of Arts in June, 1908. During the two years, 1907-1909, he acted as Demonstrator in Chemistry at Acadia University and in June 1909 received the degree of Bachelor of Science. In the fall of 1909 he entered Columbia University with advanced standing in the Chemical Engineering course. After September, 1911, the work leading to the degree of Doctor of Philosophy was carried on jointly with the work in Applied Science. From February, 1910, to June, 1911, he held the J. Pierpont Morgan scholarship in Applied Science. During the year 1910-11 he acted as Assistant in Quantitative Analysis, and during the following year held a similar position in Industrial Chemistry. In the spring of 1912 he was appointed Samuel Anthony Goldschmidt Fellow in Chemistry. In February he was graduated from the Schools of Mines, Engineering and Chemistry with the degree of Chemical Engineer.



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